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A method for the practical determination of the absolute concentration of single ($a^1\Delta_g$) oxygen is discussed. The method is based on sensitive off-axis integrated-cavity-output spectroscopy (ICOS). Off-axis ICOS allows narrowband, continuous-wave lasers to be used in conjunction with optical cavities to record sensitive absorption measurements. The details of the method as well as spectroscopic data confirming the first observation of the (1,0) band of the $b^1\Sigma_g^+ - a^1\Delta_g$ Noxon system are presented. The absolute transition probabilities for the $b^1\Sigma_g^+ - a^1\Delta_g$ Noxon system, which are not known precisely from experiments, are determined by quantum chemistry theory. © 2004 Optical Society of America

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Quantitative detection of single O_2 by cavity-enhanced absorption

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A method for the practical determination of the absolute concentration of single ($a^1\Delta_g$) oxygen is discussed. The method is based on sensitive off-axis integrated-cavity-output spectroscopy (ICOS). Off-axis ICOS allows narrowband, continuous-wave lasers to be used in conjunction with optical cavities to record sensitive absorption measurements. The details of the method as well as spectroscopic data confirming the first observation of the (1,0) band of the $b^1\Sigma_g^+ - a^1\Delta_g$ Noxon system are presented. The absolute transition probabilities for the $b^1\Sigma_g^+ - a^1\Delta_g$ Noxon system, which are not known precisely from experiments, are determined by quantum chemistry theory. © 2004 Optical Society of America

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Oxygen has systems in the near-infrared ($a^1\Delta_g - X^3\Sigma_g^-$) and the visible ($b^1\Sigma_g^+ - X^3\Sigma_g^-$) regions that are atypically weak but are important to the radiative properties of the atmosphere. As a result, these transitions are well characterized spectroscopically and are the focus of much recent work.¹⁻³ The near-infrared band system has been used to detect singlet ($a^1\Delta_g$) oxygen in a variety of environments and experiments.⁴ In addition, techniques based on spontaneous Raman scattering,⁵ vacuum-ultraviolet absorption,⁴ and electron parametric resonance detection⁴ have been used with some success. However, no method exists that can both detect and quantify singlet oxygen in a straightforward fashion. Absorption spectroscopy provides an appealing alternative, and sensitive absorption-based laser techniques are available, including direct-absorption spectroscopy using long-path multipass cells,⁶ wavelength-modulation spectroscopy,⁷ cavity-ringdown spectroscopy,⁸ cavity-enhanced absorption spectroscopy,⁹ integrated cavity-output spectroscopy (ICOS),¹⁰ and recently, off-axis ICOS.¹¹ In this Letter, off-axis ICOS is used to quantitatively detect the $a^1\Delta_g$ state of O_2 through the hitherto unobserved (1,0) band of the $b^1\Sigma_g^+ - a^1\Delta_g$ Noxon¹² system. This approach allows for the quantitative detection of singlet O_2 with a minimum detectable density of 4×10^{13} molecules cm^{-3} at 298 K, corresponding to 3×10^{12} molecules cm^{-3} per quantum state [signal/noise ratio (SNR) of 1].

Singlet oxygen was generated in a 13.56-MHz rf inductively coupled plasma by passing a 5% oxygen/95% helium mixture through a 25-mm quartz tube and coupling 250 W of rf power into the gas. The resultant afterglow passed through a 20-cm Teflon coupling and through the off-axis ICOS measurement system at ~3000 SCCM (SCCM denotes cubic centimeters per minute at STP) and a total pressure of 32 Torr. The off-axis ICOS system consisted of an 82-cm-long high-finesse optical cavity bounded by two highly reflective mirrors ($R = 99.9986\%$). The mirror

reflectivity was determined by performing a cavity-ringdown measurement^{8,11} and observing a ringdown time of 197 ms. The entire cavity was quartz coated to help prevent the deactivation of singlet oxygen. Off-axis ICOS was described previously,¹¹ and a similar methodology was employed here. Briefly, a single-mode, fiber-pigtailed distributed-feedback diode laser (1505 nm, 0.0001- cm^{-1} bandwidth) was coupled into the optical cavity in an off-axis alignment that was optimized to maximize the light's reentrant condition and to minimize coherent interferences. The laser was temperature controlled to set its central wavelength and then current tuned over ~ 0.33 cm^{-1} at 25–50 Hz. Typically 5000–10,000 spectra were obtained, corresponding to ~ 5 min of averaging. Light exiting the cavity was focused onto an InGaAs detector, and the cavity transmission was recorded as a function of laser frequency. The absorption within the cavity leads to a decrease in transmitted intensity, ΔI , given by $\Delta I/I_0 = GA/(1 + GA)$, where I_0 is the incident laser intensity, A is the single-pass absorption, and $G = R/(1 - R)$ is the cavity-enhancement factor.^{10,11} For the cavity used in this study, $G = 72,100 \pm 180$. The exact laser frequency and tuning rate were determined by use of known water absorption features and a calibrated SiO_2 etalon as described below.

Near-infrared emission from a low-pressure helium discharge seeded with 0.5% O_2 was observed by Noxon in 1961 and subsequently assigned by him to the $b^1\Sigma_g^+ - a^1\Delta_g$ (0,0) transition in O_2 .¹² Noxon recorded a broad feature at 1.908 μm (7.0-nm slit width used in the experiment), which he attributed to the unresolved Q-branch transitions of the (0,0) band of the $b^1\Sigma_g^+ - a^1\Delta_g$ system. Despite the early discovery of this spectroscopic system, there are only two other reported observations of this transition^{13,14} and no other comprehensive measurements of the absolute strengths of spectral lines and shifts or widths of individual lines. The first of these papers appeared in 1985, where Fink *et al.*¹³ repeated Noxon's experiment

with much higher spectral resolution and observed resolved O -, P -, Q -, R -, and S -branch transitions of the b - a system and confirmed that the relative intensities agree with those calculated for an electric quadrupole transition. In 2001, Pazyuk *et al.*¹⁴ detected select Q -branch transitions of the $(0,0)$ band of the b - a system, using intracavity laser spectroscopy. A minimum detectable density of 3.5×10^{14} molecules cm^{-3} (SNR of 1) was reported by Pazyuk *et al.*, which, using their reported temperature of 305 K, corresponds to 3×10^{13} molecules cm^{-3} per quantum state. This Letter reports what is believed to be the first observation of the much weaker but experimentally more accessible $(1,0)$ band of the Noxon system via sensitive off-axis ICOS absorption spectroscopy.

Figure 1 shows three spectra recorded under different conditions. The ambient water spectrum is taken after the off-axis ICOS cell is filled with ~ 5 Torr of ambient laboratory air. The lines appearing in the spectrum are assigned to known water transitions by use of the HITRAN96 database.¹⁵ The cell is then evacuated, and a rf discharge is initiated at a pressure of 30.4-Torr helium gas and with a mass flow rate of ~ 3000 SCCM. This spectrum is labeled He Plasma, and no absorption lines are observed in this region of the spectrum. The addition of 1.5 Torr of oxygen gas results in a peak appearing at 6641.29 cm^{-1} when we use the water line calibration spectrum shown in Fig. 1(a), which is within 0.01 cm^{-1} of the calculated position based on the spectroscopic data.³ These same spectral data were used to predict the position of the Q -branch transitions shown in Fig. 2 and selected P -branch transitions. All observed line positions are within 0.01 cm^{-1} of the predicted values.

The line-strength factors for this transition were derived by Chiu¹⁶ and experimentally verified for the $(0,0)$ band by emission in the work of Fink *et al.*¹³ These line-strength factors are used to produce the fitted spectrum in Fig. 2. The entire Q branch is fitted simultaneously with Voigt line shapes with common Doppler width but varying Lorentzian widths. The line strengths are taken from Chiu,¹⁶ and the only adjustable parameters are the temperature and the individual Lorentzian widths. As can be seen from Fig. 2, the simulation is good, yielding a temperature of $317 \pm 1 \text{ K}$. Numerically integrating the peaks in the spectrum and performing a Boltzmann analysis yielded a temperature of $312 \pm 14 \text{ K}$.

In this experiment the plasma in the absorption cell is still energetic. In absorption, the transitions assigned to the OH radical were observed, presumably from the trace amount of water entrained into the helium from the polypropylene transfer lines. Hot water bands were also observed in the spectrum. Despite the high degree of excitation, the rotational temperature is quite low. The experiment was repeated by passing the plasma gases through approximately 1 cm of densely packed quartz wool, reducing the signal by 20%. Neither atomic oxygen emission lines nor OH and hot water absorption features were present in the spectrum. The singlet O_2 rotational temperature in these experiments obtained from a Boltzmann analysis of the integrated spectral peaks was $297 \pm 12 \text{ K}$, which

is within 1 K of the cell temperature as measured by a thermocouple.

Figure 3 shows a high-resolution Voigt fit of the $Q(8)$ transition. As can be seen from the figure, the Voigt profile reproduces the line shape well. Using the temperature from the fitted spectrum of Fig. 2 and free fitting the Lorentzian width yield a homogeneous full width at half-maximum of $0.0038 \pm 0.0004 \text{ cm}^{-1}$. Linewidths of the $(0,0)$ band of the $a^1\Delta_g$ - $X^3\Sigma_g^-$ transition¹⁻³ and the $(1,0)$ band of the $b^1\Sigma_g^+$ - $X^3\Sigma_g^-$ transition^{3,17} have been measured as well as the pure rotation lines of the $a^1\Delta_g$ state¹ and the $X^3\Sigma_g^-$ state.¹⁸ Note that the pressure-broadening coefficients in the literature are reported mainly for O_2 and N_2 , and the bulk of the gas used in our experiments is helium. However, Setzer and Pickett¹⁸ found that the pressure-broadening coefficient for the pure rotation ground state $X^3\Sigma_g^- N = 7 \leftarrow 6$ line for collisions with helium to be 75% that of O_2 and N_2 . If the assumption is made that the pressure broadening of a rotational line can be taken as the mean of the values for the upper and lower states with comparable coefficients for O_2 and helium, then the linewidth calculated for the $Q(8)$ line of the $b^1\Sigma_g^+$ - $a^1\Delta_g$ $(1,0)$ transition

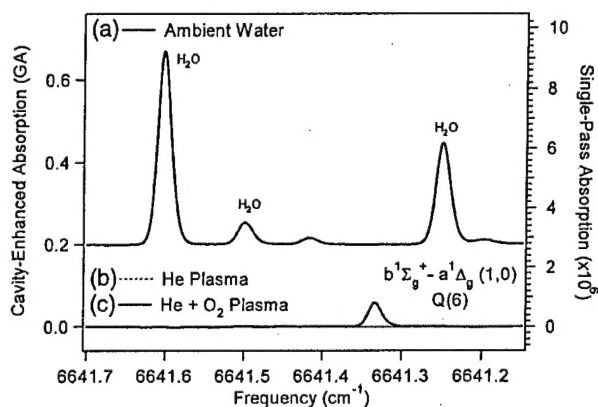


Fig. 1. Cavity-enhanced absorption (GA) measurement in the region of the $Q(6)$ line of the $b^1\Sigma_g^+$ - $a^1\Delta_g$ $(1,0)$ transition recorded for three different gas compositions: (a) 5-Torr ambient air, (b) flowing afterglow of a helium rf discharge, (c) discharge of (b) seeded with 5% O_2 . Spectrum (a) is offset by 0.2 absorption units.

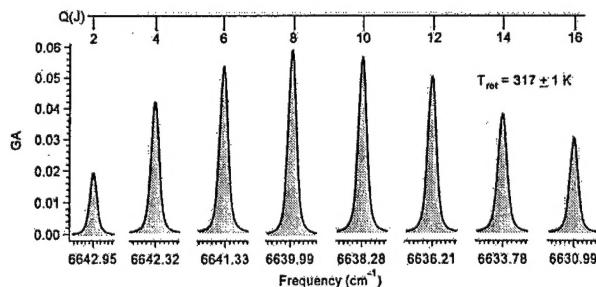


Fig. 2. Cavity-enhanced absorption (GA) measurement of $\text{O}_2 a^1\Delta_g$ obtained by tuning the diode laser over selected Q -branch transitions at a scan rate of 25 Hz. The gray areas are the data, and the solid curves are the fitted spectrum, yielding a rotational temperature of $317 \pm 1 \text{ K}$ (see text).

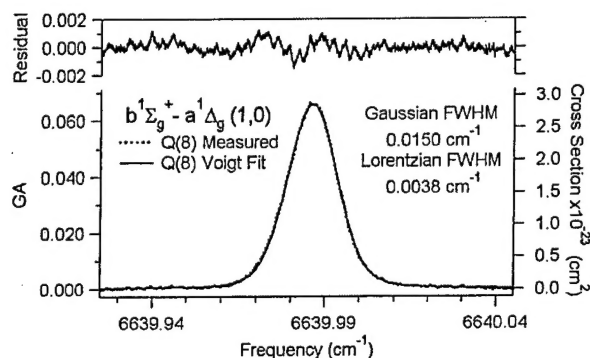


Fig. 3. Cavity-enhanced absorption (GA) measurement of O_2 $a^1\Delta_g$ obtained by tuning the diode laser over the $Q(8)$ transition. The dotted curve is the data, and the solid curve is the result of a Voigt fit to the baseline-corrected peak shape. The right-hand axis is the calculated cross section (see text).

at our conditions ranges from 0.0034 to 0.0045 cm^{-1} , which is in excellent agreement with the fitted result.

The absolute transition probability of the $b^1\Sigma_g^+ - a^1\Delta_g$ (0,0) transition was estimated by Noxon¹² to within a factor of 2 to be $2.5 \times 10^{-3} s^{-1}$. The numerical value used today is based on a more recent value of A coefficient for the $b-X$, (0,0) deduced by Burch and Gryvnak,¹⁹ yielding a value of $1.7 \times 10^{-3} s^{-1}$. However, an additional correction should be made at this point because Noxon assumed that the Q branch represented one fifth of the total band intensity. In light of the line-strength factors derived by Chiu¹⁶ and verified by Fink *et al.*,¹³ the Q branch actually represents approximately one third of the band intensity. Therefore, the A coefficient measured by Noxon should be scaled down by a factor of 3/5 yielding a value of $1.0 \times 10^{-3} s^{-1}$.

The $b-a$ transition is electric dipole forbidden and will have a weak electric quadrupole transition moment, and the transition probability will be determined from the quadrupole moment. In the absence of sufficient experimental data, the quadrupole transition moment has been computed with *ab initio* quantum theory. Specifically, the rovibrational Schrödinger equation was solved in the case b limit. The computed potential energy curves yielded vibronic energy levels in excellent agreement with experiment. These solutions to the nuclear Schrödinger equation were used to construct the state-to-state quadrupole transition moments. These calculations yield a value of $1.3 \times 10^{-3} s^{-1}$ for the A coefficient for the (0,0) band in the $b^1\Sigma_g^+ - a^1\Delta_g$ system, in excellent agreement with Noxon's value and confirming the pure electric quadrupole nature of the transition. The quantum theory results are used to calculate the cross section for the $Q(8)$ transition of the (1,0) band shown in Fig. 3.

Using the theoretical value for the cross section shown in Fig. 3 and the fitted rotational temperature, we obtained a concentration of singlet oxygen of 4×10^{14} molecules cm^{-3} per quantum state (12% conversion efficiency) in the discharge. The line spectrum shown in Fig. 3 has a SNR of 150, and using the obtained concentration yields a detection limit,

SNR of 1, for singlet O_2 of $3 \times 10^{12} cm^{-3}$ per quantum state. Thus sensitive detection of singlet oxygen via the $b^1\Sigma_g^+ - a^1\Delta_g$ (1,0) transition has been demonstrated by use of off-axis ICOS spectroscopy. This study also reports the first observation of the (1,0) vibronic band of the Noxon system. The measured absolute line positions and linewidths are in excellent agreement with those calculated from available spectroscopic data of the $a^1\Delta_g - X^3\Sigma_g^-$ (0,0) transition and the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ (1,0) transition. Theoretical calculations confirm that the transition is electric quadrupole and the *ab initio* transition probabilities are in excellent agreement with the values obtained by Noxon. Consequently, this method should permit the absolute determination of singlet oxygen concentrations in a variety of environments.

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